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(54) Title: DRY CLEANING WITH ENZYMES (57) Abstract Enzymes are used in a dry cleaning composition and process. Cleaning compositions comprising lipase, protease and/or amylase enzymes are applied to soiled fabrics in the presence of an organic solvent such as butoxy propoxy propanol to clean the fabrics. In a preferred mode, an enzyme-containing dry cleaning composition is releasably contained in a sheet substrate. The sheet is tumbled with soiled fabrics in a conventional home clothes dryer to clean soiled garments.		

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DRY CLEANING WITH ENZYMES

FIELD OF THE INVENTION

The present invention relates to the use of enzymes in dry cleaning processes and compositions which are especially adapted for use in the home.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of co-pending application Serial No. 08/493,195, filed June 20, 1995.

BACKGROUND OF THE INVENTION

By classical definition, the term "dry cleaning" has been used to describe processes for cleaning textiles using nonaqueous solvents. Dry cleaning is an old art, with solvent cleaning first being recorded in the United Kingdom in the 1860's. Typically, dry cleaning processes are used with garments such as woolens which are subject to shrinkage in aqueous laundering baths, or which are judged to be too valuable or too delicate to subject to aqueous laundering processes. Various hydrocarbon and halocarbon solvents have traditionally been used in dry cleaning processes due to their ability to dissolve and remove oily soils and stains. However, the need to handle and reclaim such solvents has mainly restricted the practice of conventional dry cleaning to commercial establishments.

While solvent-based dry cleaning processes are reasonably effective for removing oily stains from fabrics, they are not optimal for removing particulates such as clay soils, and may require special treatment conditions to remove proteinaceous stains. Traditionally, particulates and proteinaceous stains are removed from fabrics using detergent ingredients and operating conditions which are more akin to aqueous laundering processes than to conventional dry cleaning.

In addition to the cleaning function, dry cleaning also provides important "refreshment" benefits. For example, dry cleaning removes undesirable odors and extraneous matter such as hair and lint from garments, which are then generally folded or pressed to remove wrinkles and restore their original shape. Of course, such refreshment benefits are also afforded by aqueous laundering processes.

As can be seen from the foregoing, and aside from the effects on certain fabrics such as woolens, there are no special, inherent advantages for solvent-based immersion dry cleaning over aqueous cleaning processes with respect to fabric cleaning or refreshment. Moreover, on a per-garment basis, commercial dry cleaning is much more expensive than aqueous cleaning processes.

There has been a continuing search for new, safe and environmentally acceptable solvents for use in dry cleaning. Unfortunately, many such solvents are expensive and, as noted, require a recycling apparatus to provide for their recovery and re-use. In any event, such solvents function merely as a result of their ability to dissolve oily stains, and are thus somewhat limited in their cleaning power.

The present invention employs a novel approach to the dry cleaning operation. Succinctly stated, in the present process enzymes are used to degrade soils and stains, thereby enhancing their removal. For example, while conventional dry cleaning uses only solvents, or solvent/surfactant mixtures, to dissolve or emulsify, and only incompletely remove, stains such as the lipids present in foods, the use of lipase enzymes according to the present invention fragments the lipids into smaller, more soluble molecules, thereby enhancing their likelihood of removal.

Accordingly, it is an object of the present invention to provide dry cleaning compositions and processes which employ enzymes such as lipases, proteases, amylases and mixtures thereof, to degrade lipids, proteinaceous soils and saccharidic soils, respectively. It is another object herein to provide dry cleaning compositions and processes which are suitable for in-home use. It is another object herein to provide non-immersion dry cleaning compositions and processes. These and other objects are secured herein, as will be seen from the following disclosure.

BACKGROUND ART

Dry cleaning processes are disclosed in: EP 429,172A1, published 29.05.91, Leigh, et al.; and in U.S. 5,238,587, issued 8/24/93, Smith, et al. Other references relating to dry cleaning compositions and processes, as well as wrinkle treatments for fabrics, include: GB 1,598,911; and U.S. Patents 4,126,563, 3,949,137, 3,593,544, 3,647,354; 3,432,253 and 1,747,324; and German applications 2,021,561 and 2,460,239, 0,208,989 and 4,007,362. Cleaning/pre-spotting compositions and methods are also disclosed, for example, in U.S. Patents 5,102,573; 5,041,230; 4,909,962; 4,115,061; 4,886,615; 4,139,475; 4,849,257; 5,112,358; 4,659,496; 4,806,254; 5,213,624; 4,130,392; and 4,395,261. Sheet substrates for use in a laundry dryer are disclosed in Canadian 1,005,204. U.S. 3,956,556 and 4,007,300 relate to perforated sheets for fabric conditioning in a clothes dryer. U.S. 4,692,277 discloses the use of 1,2-octanediol in liquid cleaners. See also U.S. Patents 3,591,510; 3,737,387; 3,764,544; 3,882,038; 3,907,496; 4,097,397; 4,102,824; 4,336,024; 4,606,842; 4,758,641; 4,797,310; 4,802,997; 4,943,392; 4,966,724; 4,983,317; 5,004,557; 5,062,973; 5,080,822; 5,173,200; EP 0 213 500; EP0 261 718; G.B. 1,397,475; WO 91/09104; WO 91/13145; WO 93/25654 and Hunt, D.G. and N.H. Morris, "PnB and DPnB Glycol Ethers", HAPPI, April 1989, pp. 78-82.

SUMMARY OF THE INVENTION

The present invention encompasses a dry cleaning and spot removal composition, comprising:

- (a) at least about 0.001%, by weight, of a deterative enzyme, especially a lipase, but also members selected from the group consisting of proteases and amylases, and mixtures of such enzymes;
- (b) from about 1% to about 30%, by weight, of an organic cleaning solvent;
- (c) optionally, at least about 0.01%, by weight, of a polyacrylate emulsifier;
- (d) optionally, from about 0.05% to about 5%, by weight, of deterative surfactants;

and

(e) water.

The organic solvent used herein is preferably a member selected from the group consisting of butoxy propoxy propanol (BPP; preferred herein), methoxy propoxy propanol (MPP), ethoxy propoxy propanol (EPP), propoxy propoxy propanol (PPP), and mixtures and all isomers thereof, although other solvents may be used. The polyacrylate emulsifier is available commercially from a variety of sources, and preferably has a molecular weight in the range from about 100,000 to about 10,000,000.

The compositions herein optionally can also comprise a deterative surfactant which is preferably a member selected from the group consisting of amine oxides, alkyl ethoxy sulfates, and mixtures thereof. The alkyl ethoxy sulfate surfactants are preferably in their magnesium salt form.

In yet another mode, the compositions herein additionally comprise at least about 0.05%, by weight, of 1,2-octanediol as a highly preferred wetting agent.

The invention also encompasses a method for cleaning fabrics, comprising applying to said fabrics a composition according to the present invention, and especially wherein said method is at least partly conducted in a hot air clothes dryer.

The invention also encompasses an article for cleaning fabrics comprising a carrier, preferably an integral carrier, releasably containing an amount of the cleaning composition herein sufficient to clean a designated load of soiled fabrics, i.e., typically from about 5-50 grams of composition per kilogram of fabrics.

All percentages, ratios and proportions herein are by weight, unless otherwise specified. All documents cited are, in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

The ingredients of the dry cleaning compositions and their use in the process of the present invention are described *serialim* hereinafter.

Cleaning Compositions - The chemical compositions which are used to provide the cleaning function in the present dry cleaning process comprise ingredients which are safe and effective for their intended use. Since the process herein does not involve an aqueous rinse step, the cleaning compositions employ ingredients which do not leave undesirable residues on fabrics when employed in the manner disclosed herein. Moreover, since the process may be carried out in a hot air clothes dryer, the compositions contain only ingredients whose flash points render them safe for such use. The cleaning compositions preferably do contain some water, since water not only aids in the cleaning function, but also can help remove wrinkles and restore fabric drape and appearance, especially in hot air dryers. While conventional laundry detergents are typically formulated to provide good cleaning on cotton and cotton/polyester blend fabrics, the cleaning compositions herein must be formulated to safely and effectively clean and refresh fabrics such as wool, silk, rayon, rayon acetate, and the like.

In addition, the cleaning compositions herein comprise ingredients which are specially selected and formulated to minimize dye removal from the fabrics being cleaned. In this regard, it is recognized that the solvents typically used in immersion dry cleaning processes can remove some portion of certain types of dyes from certain types of fabrics. However, such removal is tolerable in immersion processes since the dye is removed relatively uniformly across the surface of the fabric. In contrast, it has now been determined that high concentrations of certain types of cleaning ingredients at specific sites on fabric surfaces can result in unacceptable localized dye removal. The preferred cleaning compositions herein are formulated to minimize or avoid this problem.

The dye removal attributes of the present cleaning compositions can be compared with art-disclosed cleaners using photographic or photometric measurements, or by means of a simple, but effective, visual grading test. Numerical score units can be assigned to assist in visual grading and to allow for statistical treatment of the data, if desired. Thus, in one such test, a colored garment (typically, silk, which tends to be more susceptible to dye loss than most woolen or rayon substrates) is treated by padding-on cleaner using an absorbent, white paper hand towel. Hand pressure is applied, and the amount of dye which is transferred onto the white towel is assessed visually. Numerical units ranging from: (1) "I think I see a little dye on the towel"; (2) "I know I see some dye on the towel"; (3) "I see a lot of dye on the towel"; through (4) "I know I see quite a lot of dye on the towel" are assigned by panelists.

Having due regard to the foregoing considerations, the following illustrates the ingredients used in the cleaning compositions herein, but is not intended to be limiting thereof.

- (a) Enzyme - The compositions herein comprise enzymes at levels sufficient to provide up to about 5 mg by weight, more typically about 0.001 mg to about 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from about 0.001% to about 5%, preferably 0.01%-1% by weight of commercial lipase, protease and amylase enzyme preparations, or mixtures thereof.
- (b) Solvent - The compositions will most preferably comprise at least about 4%, typically from about 5% to about 25%, by weight, of the solvent. The objective is to provide at least about 0.4 g, preferably from about 0.5 g to about 2.5 g, of solvent per kg of fabrics being cleaned.
- (c) Emulsifier - The compositions will most preferably comprise sufficient polyacrylate emulsifier to provide a stable, homogeneous composition comprising components (a), (b) and (d). For the emulsifiers disclosed herein, levels as low as 0.05%, preferably 0.07% to about 0.20%, by weight are effective. Levels above about 0.2% are unnecessary and are preferably not used, thereby avoiding residues on fabrics.
- (d) Water - The compositions will comprise at least about 60%, typically from about

80% to about 95%, by weight, of water. Stated otherwise, the objective is to provide at least about 6 g of water per kg of fabrics being cleaned.

- (e) Optionals - The compositions herein may comprise various optional ingredients, including perfumes, conventional surfactants, carriers and the like. If used, such optional ingredients will typically comprise from about 0.1% to about 10%, by weight, of the compositions, having due regard for residues on the cleaned fabrics.

Enzymes are incorporated in the formulations herein to enhance and provide superior fabric cleaning, including removal of protein-based, carbohydrate-based, or lipid (triglyceride-based) stains. The enzymes to be incorporated include lipases, proteases and amylases, as well as mixtures thereof. The enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin.

Suitable lipase enzymes for use herein include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open to public inspection on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. The LIPOLASE enzyme derived from *Humicola lanuginosa* and commercially available from Novo (see also EPO 341,947) is a preferred lipase for use herein.

Suitable protease enzymes are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE and SAVINASE by Novo Industries A/S (Denmark) and MAXATASE by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985) and Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al, published January 9, 1985). Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Amylases include, for example, α -amylases described in British Patent Specification No.

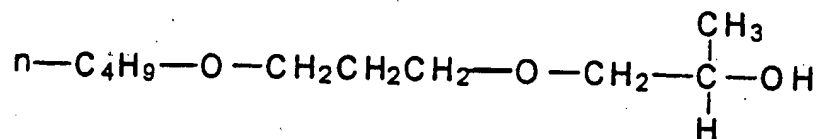
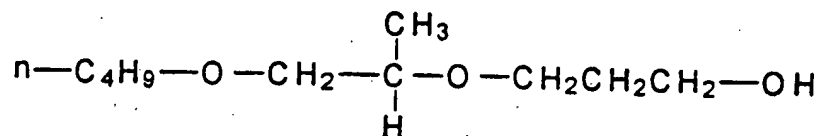
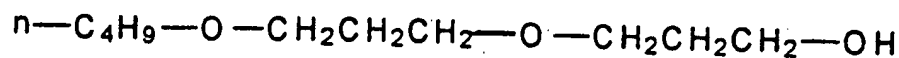
1,296,839 (Novo), RAPIDASE, International Bio-Synthetics, Inc. and TERMAMYL, Novo Industries.

A wide range of suitable enzymes are also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al, issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985; and also in U.S. Patent 4,261,868, Hora et al, issued April 14, 1981. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al, and European Patent Application Publication No. 0 199 405, Application No. 86200586.5, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. Patent 3,519,570.

The enzymes employed herein can be stabilized by the presence of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. (Calcium ions are generally somewhat more effective than magnesium ions and are preferred herein if only one type of cation is being used.) Additional stability can be provided by the presence of various other art-disclosed stabilizers, especially borate species: see Severson, U.S. 4,537,706. Cleaning compositions with stabilized enzymes typically comprise from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 5 to about 15, and most preferably from about 8 to about 12, millimoles of calcium ion per liter of finished composition. This can vary somewhat, depending on the amount of enzyme present and its response to the calcium or magnesium ions. Any water-soluble calcium or magnesium salt can be used as the source of calcium or magnesium ions, including, but not limited to, calcium chloride, calcium sulfate, calcium malate, calcium maleate, calcium hydroxide, calcium formate, and calcium acetate, and the corresponding magnesium salts. A small amount of calcium ion, generally from about 0.05 to about 0.4 millimoles per liter, is often also present in the composition due to calcium in the enzyme slurry and formula water. In some instances, this may be sufficient to provide the desired stability. In any event, the selection and use of the stabilizer is a matter of routine.

In an alternative mode, the enzymes may be "spotted" onto various discrete areas of the carrier used herein. This allows the formulator to improve enzyme stability by isolating individual enzymes from other, potentially de-stabilizing, ingredients which may be present in the cleaning compositions used herein. For example, lipase enzymes may be spotted separately from protease enzymes, etc.

The preferred solvent herein is butoxy propoxy propanol (BPP) which is available in commercial quantities as a mixture of isomers in about equal amounts. The isomers, and mixtures thereof, are all useful herein. The isomer structures are as follows. (The MPP, EPP and PPP solvents also exist as isomers and isomer mixtures, all of which are useful herein.)



BPP is outstanding for cleaning, and is so effective that it allows the amount of the relatively expensive 1,2-octanediol to be minimized. Moreover, it allows for the formulation of effective cleaning compositions herein without the use of conventional surfactants. Importantly, the odor of BPP is of a degree and character that it can be relatively easily masked by conventional perfume ingredients. While BPP is not completely miscible with water and, hence, could negatively impact processing of the cleaning compositions herein, that potential problem has been successfully overcome by means of the PEMULEN-type polyacrylate emulsifiers, in the manner disclosed hereinafter.

It has now been determined that 1,2-octanediol ("OD") affords special advantages in the formulation of the cleaning compositions herein. From the standpoint of aesthetics, OD is a relatively innocuous and low odor material. Moreover, OD appears to volatilize from fabric surfaces without leaving visible residues. This is especially important in a dry cleaning process of the present type which is conducted without a rinse step. From the performance standpoint, OD appears to function both as a solvent for greasy/oily stains and as what might be termed a "pseudo-surfactant" for particulate soils and water-soluble stains. Whatever the physical-chemical reason, OD has now been found to be a superior wetting agent with respect to both cleaning and ease-of-use in the present context of home-use cleaning compositions and processes. If used, OD will typically comprise from about 0.1% to about 1.5% of the cleaning compositions herein.

The BPP solvent used herein is preferably a mixture of the aforesaid isomers. In a preferred mode, the cleaning compositions comprise a mixture of the 1,2-octanediol and BPP, at a weight ratio of OD:BPP in the range of from about 1:250 to about 2:1, preferably from about 1:200 to about 1:5. Similar ratios can be used with the MPP, EPP and PPP solvents.

The highly preferred emulsifier herein is commercially available under the trademark PEMULEN, The B. F. Goodrich Company, and is described in U.S. Patents 4,758,641 and 5,004,557, incorporated herein by reference. PEMULEN polymeric emulsifiers are high molecular weight polyacrylic acid polymers. The structure of PEMULEN includes a small portion that is oil-loving (lipophilic) and a large water-loving (hydrophilic) portion. The structure allows PEMULEN to function as a primary oil-in-water emulsifier. The lipophilic portion adsorbs at the oil-water interface, and the hydrophilic portion swells in the water forming a network around the oil droplets

t provide emulsion stability. An important advantage for the use of such polyacrylate emulsifiers herein is that cleaning compositions can be prepared which contain solvents or levels of solvents that are otherwise not soluble or readily miscible with water. A further advantage is that effective emulsification can be accomplished using PEMULEN-type emulsifier at extremely low usage levels (0.05-0.2%), thereby minimizing the level of any residue left on fabrics following product usage. For comparison, typically about 3-7% of conventional anionic or nonionic surfactants are required to stabilize oil-in-water emulsions, which increases the likelihood that a residue will be left on the fabrics. Another advantage is that emulsification (processing) can be accomplished effectively at room temperature.

While the cleaning compositions herein function quite well with only the enzyme, the 1,2-octanediol, BPP, PEMULEN and water, they may also optionally contain deterative surfactants to further enhance their cleaning performance. While a wide variety of deterative surfactants such as the C₁₂-C₁₆ alkyl sulfates and alkylbenzene sulfonates, the C₁₂-C₁₆ ethoxylated (EO 0.5-10 avg.) alcohols, the C₁₂-C₁₄ N-methyl glucamides, and the like can be used herein, it is highly preferred to use surfactants which provide high grease/oil removal. Included among such preferred surfactants are the C₁₂-C₁₆ alkyl ethoxy sulfates (AES), especially in their magnesium salt form, and the C₁₂-C₁₆ dimethyl amine oxides. Especially preferred mixtures comprise MgAE₁S/MgAE_{6.5}S/C₁₂ dimethyl amine oxide, at a weight ratio of about 1:1:1, and MgAE₁S/C₁₂ dimethyl amine oxide at a 2:1 weight ratio. If used, such surfactants will typically comprise from about 0.05% to about 2.5%, by weight, of the cleaning compositions herein.

In addition to the preferred solvents and emulsifiers disclosed above, the cleaning compositions herein may comprise various optional ingredients, such as perfumes, preservatives, co-solvents, brighteners, salts for viscosity control, pH adjusters or buffers, anti-static agents, softeners, colorants, mothproofing agents, insect repellents, and the like.

Carrier - When used in a dry cleaning operation, the cleaning compositions are preferably used in combination with a carrier, such that the cleaning composition performs its function as the surfaces of the fabrics being cleaned come in contact with the surface of the carrier.

The carrier can be in any desired form, such as powders, flakes, shreds, and the like. However, it will be appreciated that such comminuted carriers would have to be separated from the fabrics at the end of the cleaning process. Accordingly, it is highly preferred that the carrier be in the form of an integral pad or sheet which substantially maintains its structural integrity throughout the cleaning process. Such pads or sheets can be prepared, for example, using well-known methods for manufacturing non-woven sheets, paper towels, fibrous batts, cores for bandages, diapers and catamenials, and the like, using materials such as wood pulp, cotton, rayon, polyester fibers, and mixtures thereof. Woven cloth pads may also be used, but are not preferred over non-woven pads due to cost considerations. Integral carrier pads or sheets may also be prepared from natural or synthetic sponges, foams, and the like.

The carriers are designed to be safe and effective under the intended operating conditions of the present process. The carriers must not be flammable during the process, nor should they deleteriously interact with the cleaning composition or with the fabrics being cleaned. In general, non-woven polyester-based pads or sheets are quite suitable for use as the carrier herein.

5 The carrier used herein is most preferably non-linting. By "non-linting" herein is meant a carrier which resists the shedding of visible fibers or microfibers onto the fabrics being cleaned, i.e., the deposition of what is known in common parlance as "lint". A carrier can easily and adequately be judged for its acceptability with respect to linting by rubbing it on a piece of dark blue woolen cloth and visually inspecting the cloth for lint residues.

10 The non-linting sheet or pad carriers used herein can be prepared by several means, including but not limited to: preparing the carrier from a single strand of fiber, employing known bonding techniques commonly used with nonwoven materials, e.g., point bonding, print bonding, adhesive/resin saturation bonding, adhesive/resin spray bonding, stitch bonding and bonding with binder fibers. In an alternate mode, a carrier can be prepared using an absorbent core, said core
15 being made from a material which, itself, may shed lint. The core is then enveloped within a sheet of porous, non-linting material having a pore size which allows passage of the cleaning compositions, but through which lint from the core cannot pass. An example of such a carrier comprises a cellulose or polyester fiber core enveloped in a non-woven polyester scrim.

The carrier should be of a size which provides sufficient surface area that effective contact
20 between the surface of the carrier and the surface of the fabrics being cleaned is achieved. Of course, the size of the carrier should not be so large as to be unhandy for the user. Typically, the dimensions of the carrier will be sufficient to provide a macroscopic surface area (both sides of the carrier) of at least about 360 cm^2 , preferably in the range from about 360 cm^2 to about 3000 cm^2 . For example, a rectangular carrier may have the dimensions (x-direction) of from about 20 cm to
25 about 35 cm, and (y-direction) of from about 18 cm to about 45 cm.

The carrier is intended to contain a sufficient amount of the cleaning composition to be effective for its intended purpose. The capacity of the carrier for the cleaning composition will vary according to the intended usage. For example, carrier/cleaning composition pads or sheets which are intended for a single use will require less capacity than such pads or sheets which are intended
30 for multiple uses. For a given type of carrier the capacity for the cleaning composition will vary mainly with the thickness or "caliper" (z-direction; dry basis) of the sheet or pad. For purposes of illustration, typical single-use polyester sheets used herein will have a thickness in the range from about 0.1 mm to about 0.7 mm and a basis weight in the range from about 30 g/m^2 to about 100 g/m^2 . Typical multi-use polyester pads herein will have a thickness in the range from about
35 0.2 mm to about 1.0 mm and a basis weight in the range from about 40 g/m^2 to about 150 g/m^2 . Open-cell sponge sheets will range in thickness from about 0.1 mm to about 1.0 mm. Of course, the foregoing dimensions may vary, as long as the desired quantity of the cleaning composition is

effectively provided by means of the carrier.

The preferred carrier herein comprises a binderless (or optional low binder), hydroentangled absorbent material, especially a material which is formulated from a blend of cellulosic, rayon, polyester and optional bicomponent fibers. Such materials are available from
 5 Dexter, Non-Wovens Division, The Dexter Corporation as HYDRASPUN®, especially Grade 10244. The manufacture of such materials forms no part of this invention and is already disclosed in the literature. See, for example, U.S. Patents 5,009,747, Viazmensky, et al., April 23, 1991 and 5,292,581, Viazmensky, et al., March 8, 1994, incorporated herein by reference. Preferred materials for use herein have the following physical properties.

	Grade		Optional
	<u>10244</u>	<u>Targets</u>	<u>Range</u>
Basis Weight	gm/m ²	55	35-75
Thickness	microns	355	100-1500
Density	gm/cc	0.155	0.1-0.25
15 Dry Tensile	gm/25 mm		
MD		1700	400-2500
CD		650	100-500
Wet Tensile	gm/25 mm		
MD*		700	200-1250
20 CD*		300	100-500
Brightness	%	80	60-90
Absorption Capacity	%	735	400-900 (H ₂ O)
Dry Mullen	gm/cm ²	1050	700-1200

*MD - machine direction; CD - cross direction

25 As disclosed in U.S. 5,009,747 and 5,292,281, the hydroentangling process provides a nonwoven material which comprises cellulosic fibers, and preferably at least about 5% by weight of synthetic fibers, and requires less than 2% wet strength agent to achieve improved wet strength and wet toughness.

In addition to the improved cleaning performance, it has now been discovered that the
 30 hydroentangled carrier material used herein provides an additional, unexpected benefit due to its resiliency. In-use, the dry cleaning sheets herein are designed to function in a substantially open configuration. However, the sheets are packaged and sold to the consumer in a folded configuration. It has been discovered that carrier sheets made from conventional materials tend to undesirably revert to their folded configuration in-use. This undesirable attribute can be overcome by perforating
 35 such sheet, but this requires an additional processing step. It has now been discovered that the hydroentangled materials used to form the carrier sheet herein do not tend to re-fold during use, and thus do not require such perforations (although, of course, perforations may be used, if desired).

Accordingly, this newly-discovered and unexpected attribute of the preferred carrier materials herein makes them optimal for use in the manner of the present invention.

Container - The present cleaning process is conducted using a flexible container. The fabrics to be cleaned are placed within the container with the carrier/cleaning composition article, and the container is agitated, thereby providing contact between the carrier/cleaning composition and the surfaces of the fabrics.

The flexible container used herein can be provided in any number of configurations, and is conveniently in the form of a flexible pouch, or "bag", which has sufficient volume to contain the fabrics being cleaned. Suitable containers can be manufactured from any economical material, such as polyester, polypropylene, and the like, with the proviso that it must not melt if used in contact with hot dryer air. It is preferred that the walls of the container be substantially impermeable to water vapor and solvent vapor under the intended usage conditions. It is also preferred that such containers be provided with a sealing means which is sufficiently stable to remain closed during the cleaning process. Simple tie strings or wires, various snap closures such as ZIP LOK® closures, and VELCRO®-type closures, contact adhesive, adhesive tape, zipper-like closures, and the like, suffice.

The container can be of any convenient size, and should be sufficiently large to allow tumbling of the container and fabrics therein, but should not be so large as to interfere with the operation of the tumbling apparatus. With special regard to containers intended for use in hot air clothes dryers, the container must not be so large as to block the air vents. If desired, the container may be small enough to handle only a single shirt, blouse or sweater, or be sufficiently large to handle a man's suit.

Process - The present cleaning process can be conducted in any manner which provides mechanical agitation, such as a tumbling action, to the container with the fabrics being cleaned. If desired, the agitation may be provided manually. However, in a convenient mode a container with the carrier/cleaning composition and enveloping the soiled fabric is sealed and placed in the drum of an automatic clothes dryer. The drum is allowed to revolve, which imparts a tumbling action to the container and agitation of its contents concurrently with the tumbling. By virtue of this agitation, the fabrics come in contact with the carrier releasably containing and carrying the cleaning composition. The composition is removed to the fabrics by contact with the carrier. It is preferred that heat be employed during the process. Of course, heat can easily be provided in a clothes dryer. The tumbling and optional (but preferred) heating is carried out for a period of at least about 10 minutes, typically from about 20 minutes to about 30 minutes. The process can be conducted for longer or shorter periods, depending on such factors as the degree and type of soiling of the fabrics, the nature of the soils, the nature of the fabrics, the fabric load, the amount of heat applied, and the like, according to the needs of the user. The following illustrates a typical process in more detail, but is not intended to be limiting thereof.

EXAMPLE I

A dry cleaning article in sheet form is assembled using a sheet substrate and a cleaning composition prepared by admixing the following ingredients.

	<u>Ingredient</u>	<u>% (wt.)</u>
5	Enzyme ¹	0.5
	PEMULEN TR-1 ²	0.15
	BPP ³	7.0
	1,2-octanediol	0.5
	Surfactant Mixture ⁴	0.50
10	KOH	0.08
	Perfume	0.75
	Water and Minors ⁵	Balance

¹Available from Novo as LIPOLASE.

²PEMULEN TR-2, B. F. Goodrich, may be substituted

15 ³Isomer mixture, available from Dow Chemical Co.

⁴Mixture of MgAE₁S, MgAE_{6.5}S and C₁₂ amine oxide, in the range of 1:1:1 to 0.5:1:1. A 1:1 to 2:1 mixture of MgAE₁S/C₁₂ amine oxide can be used.

⁵Includes preservatives such as KATHON®.

20 A non-linting carrier sheet is prepared using stock HYDRASPUN® Grade 10244 fabric, described above. The fabric is cut into carrier sheets, approximately 9 in. (22.9 cm) x 10 in. (25.4 cm), i.e., 580.6 cm² sheets.

23 Grams of the above-noted cleaning composition are evenly applied to the sheet by spreading onto the sheet with a roller or spatula using hand pressure. In an alternative mode, the cleaning composition can be applied by dipping or spraying the composition onto the substrate, 25 followed by squeezing with a roller or pair of nip rollers, i.e., by "dip-squeezing" or "spray squeezing". The external surfaces of the sheet are damp but not tacky to the touch.

A dry cleaning sheet of the foregoing type is unfolded and placed flat in a plastic bag having a volume of about 25,000 cm³ together with about 2 kg of dry garments to be cleaned. The bag is closed, sealed and placed in a conventional hot-air clothes dryer. When the garments and 30 the dry cleaning sheet are placed in the bag, the air is preferably not squeezed out of the bag before closing and sealing. This allows the bag to billow, thereby providing sufficient space for the fabrics and cleaning sheet to tumble freely together. The dryer is started and the bag is tumbled for a period of 20-30 minutes at a dryer air temperature in the range from about 50°C to about 85°C. During this time, the dry cleaning sheet remains substantially in the desired open position, thereby 35 providing effective contact with the fabrics. After the machine cycle is complete, the bag and its contents are removed from the dryer, and the spent dry cleaning sheet is discarded. The plastic bag is retained for re-use. The garments are cleaned and refreshed. The water present in the cleaning

composition serves to minimize wrinkles in the fabrics.

In an alternate mode, heavily soiled areas of the fabric being cleaned can optionally be pre-treated by pressing or rubbing a fresh dry cleaning sheet according to this invention on the area. The sheet and pre-treated fabric are then placed in the container, and the dry cleaning process is conducted in the manner described herein.

The compositions prepared in the manner of this invention can also be directly applied to isolated spots and stains on fabrics in the manner of a spot remover product. The following illustrates this aspect of the invention, but is not intended to be limiting thereof.

EXAMPLE II

A spot remover composition comprises the following:

<u>Ingredients</u>	<u>% (wt.)</u>
Enzyme*	1.0
PEMULEN	0.15
BPP**	7.0
1,2-Octanediol	0.5
Perfume	0.75
Water	Balance

*1:1:1 (wt.) mixture of LIPOLASE/SAVINASE/RAPIDASE.

**May be replaced by an equivalent amount of MPP, EPP and PPP, respectively, or mixtures thereof, and mixtures thereof with BPP.

The composition is directly padded or sprayed onto spots and stains, followed by rubbing, to effect their removal. In an alternate mode, the composition can be gelled or thickened using conventional ingredients to provide a "stick-form" spot remover. The fabrics are then placed in a container together with a cleaning article as described herein and tumbled in a hot air clothes dryer. The fabrics are cleaned, refreshed and spot-free.

Having thus described and exemplified the present invention, the following further illustrates various cleaning compositions which can be formulated and used in the practice thereof.

EXAMPLE III

<u>Ingredient</u>	<u>% (wt.) Formula Range</u>
Lipase	0.001-3%
Protease	0-3%
Amylase	0-3%
BPP*	5-25%
1,2-Octanediol	0.1-7%
MgAE ₁ S	0.01-0.8%
MgAE _{6.5} S	0.01-0.8%
C ₁₂ Dimethyl Amine Oxide	0.01-0.8%

PEMULEN**	0.05-0.20%
Perfume	0.01-1.5%
Water	Balance

pH Range from about 6 to about 8.

- 5 *May be replaced by MPP, EPP or PPP. Other co-solvents which can be used herein together with the BPP, MPP, EPP and PPP primary solvents include various glycol ethers, including materials marketed under trademarks such as Carbitol, methyl Carbitol, butyl Carbitol, propyl Carbitol, hexyl Cellosolve, and the like. If desired, and having due regard for safety and odor for in-home use, various conventional chlorinated and hydrocarbon dry cleaning solvents may also be used.
- 10 Included among these are 1,2-dichloroethane, trichloroethylene, isoparaffins, and mixtures thereof. **As disclosed in U.S. Patents 4,758,641 and 5,004,557, such polyacrylates include homopolymers which may be crosslinked to varying degrees, as well as non-crosslinked. Preferred herein are homopolymers having a molecular weight in the range of from about 100,000 to about 10,000,000, preferably 200,000 to 5,000,000.
- 15 Excellent cleaning performance is secured using any of the foregoing non-immersion processes and articles to provide from about 5 g to about 50 g of the cleaning compositions per kilogram of fabric being cleaned. Use of the polyacrylate emulsifier at the indicated low levels minimizes residues on the fabrics.

EXAMPLE IV

- 20 A dry cleaning composition with reduced tendency to cause dye "bleeding" or removal from fabrics as disclosed above is as follows. The composition is used in combination with lipase, protease or amylase enzymes, or mixtures thereof, in the manner disclosed above.

	<u>INGREDIENT</u>	<u>PERCENT (wt.)</u>	<u>(RANGE)</u>
	Butoxypropoxy propanol (BPP)	7.000	4.0 - 25.0%
25	NEODOL 23 - 6.5*	0.750	0.05 - 2.5%
	1,2-Octanediol	0.500	0.1 - 10.0%
	Perfume	0.750	0.1 - 2.0%
	Pemulen TR-1	0.125	0.05 - 0.2%
	Potassium Hydroxide (KOH)	0.060	0.024 - 0.10
30	Potassium Chloride	0.075	0.02 - 0.20
	Water (distilled or deionized)	90.740	60.0 - 95.0%

Target pH = 7.0

*Shell; C₁₂-C₁₃ alcohol, ethoxylated with average EO of 6.5.

- 15-25 Grams of a composition of the foregoing type and also comprising the desired
- 35 enzymes are placed on a carrier sheet for use in the manner disclosed herein. A preferred carrier substrate comprises a binderless (or optional low binder), hydroentangled absorbent material, especially a material which is formulated from a blend of cellulosic, rayon, polyester and optional

bicomponent fibers. Such materials are available from Dexter, Non-Wovens Division, The Dexter Corporation as HYDRASPUN[®], especially Grade 10244. The manufacture of such materials forms no part of this invention and is already disclosed in the literature. See, for example, U.S. Patents 5,009,747, Viazmensky, et al., April 23, 1991 and 5,292,581, Viazmensky, et al., March 8, 1994, incorporated herein by reference. Preferred materials for use herein have the following physical properties.

	Grade		Optional
	<u>10244</u>	<u>Targets</u>	<u>Range</u>
Basis Weight	gm/m ²	55	35-75
10 Thickness	microns	355	100-1500
Density	gm/cc	0.155	0.1-0.25
Dry Tensile	gm/25 mm		
MD		1700	400-2500
CD		650	100-500
15 Wet Tensile	gm/25 mm		
MD*		700	200-1250
CD*		300	100-500
Brightness	%	80	60-90
Absorption Capacity	%	735	400-900 (H ₂ O)
20 Dry Mullen	gm/cm ²	1050	700-1200

*MD - machine direction; CD - cross direction

As disclosed in U.S. 5,009,747 and 5,292,281, the hydroentangling process provides a nonwoven material which comprises cellulosic fibers, and preferably at least about 5% by weight of synthetic fibers, and requires less than 2% wet strength agent to achieve improved wet strength and wet toughness.

Surprisingly, this hydroentangled carrier is not merely a passive absorbent for the cleaning compositions herein, but actually optimizes cleaning performance. While not intending to be limited by theory, it may be speculated that this carrier is more effective in delivering the cleaning composition to soiled fabrics. Or, this particular carrier might be better for removing soils by contact with the soiled fabrics, due to its mixture of fibers. Whatever the reason, improved dry cleaning performance is secured.

In addition to the improved cleaning performance, it has now been discovered that this hydroentangled carrier material provides an additional, unexpected benefit due to its resiliency. In-use, the dry cleaning sheets herein are designed to function in a substantially open configuration. However, the sheets are packaged and sold to the consumer in a folded configuration. It has been discovered that carrier sheets made from conventional materials tend to undesirably revert to their folded configuration in-use. This undesirable attribute can be overcome by perforating such sheet,

but this requires an additional processing step. It has now been discovered that the hydroentangled materials used to form the carrier sheet herein do not tend to re-fold during use, and thus do not require such perforations (although, of course, perforations may be used, if desired). Accordingly, this newly-discovered and unexpected attribute of the carrier materials herein makes them optimal for use in the manner of the present invention.

A sheet of the foregoing type is placed together with the fabrics to be dry cleaned in a flexible containment bag having dimensions as noted hereinabove and sealing means. In a preferred mode, the containment bag is constructed of thermal resistant film in order to provide resistance to hot spots (350°F-400°F; 177°C to 204°C) which can develop in some dryers. This avoids internal self-sealing and external surface deformation of the bag, thereby allowing the bag to be re-used.

In a preferred embodiment, 0.0025 mm to 0.0075 mm thickness nylon film is converted into a 26 inch (66 cm) x 30 in. (76 cm) bag. Bag manufacture can be accomplished in a conventional manner using standard impulse heating equipment, air blowing techniques, and the like. In an alternate mode, a sheet of nylon is simply folded in half and sealed along two of its edges.

In addition to thermally stable "nylon-only" bags, the containment bags herein can also be prepared using sheets of co-extruded nylon and/or polyester or nylon and/or polyester outer and/or inner layers surrounding a less thermally suitable inner core such as polypropylene. In an alternate mode, a bag is constructed using a nonwoven outer "shell" comprising a heat-resistant material such as nylon or polyethylene terephthalate and an inner sheet of a polymer which provides a vapor barrier. The non-woven outer shell protects the bag from melting and provides an improved tactile impression to the user. Whatever the construction, the objective is to protect the bag's integrity under conditions of thermal stress at temperatures up to at least about 400-500°F (204°C to 260°C). Nylon VELCRO®-type, ZIP-LOK®-type and/or zipper-type closures can be used to seal the bag, in-use.

Besides the optional nonionic surfactants used as a component of the enzyme-containing cleaning compositions herein, which are preferably C₈-C₁₈ ethoxylated (E01-15) alcohols or the corresponding ethoxylated alkyl phenols, the compositions herein can contain an anti-static agent, as an optional component. If used, such anti-static agents will typically comprise at least about 0.5%, typically from about 2% to about 8%, by weight, of the compositions. Preferred anti-stats include the series of sulfonated polymers available as VERSAFLEX 157, 207, 1001, 2004 and 7000, from National Starch and Chemical Company.

The compositions herein can optionally be stabilized for storage using conventional preservatives such as KATHON® at a level of 0.001%-1%, by weight.

If the compositions herein are used in a spot-cleaning mode, they are preferably pressed (not rubbed) onto the fabric at the spotted area using an applicator pad comprising looped fibers,

such as is available as APLIX 200 or 960 Uncut Loop, from Aplix, Inc., Charlotte, NC. An underlying absorbent sheet or pad of looped fibers can optionally be placed beneath the fabric in this mode of operation.

WHAT IS CLAIMED IS:

CLAIMS:

1. A dry cleaning and spot removal composition, characterized in that it comprises:
 - (a) at least 0.001%, by weight, of a deterative enzyme;
 - (b) from 1% to 30%, by weight, of an organic cleaning solvent;
 - 5 (c) optionally, at least 0.01%, by weight, of a polyacrylate emulsifier;
 - (d) optionally, from 0.05% to 5%, by weight, of deterative surfactants; and
 - (e) water.
2. A composition according to Claim 1 wherein the enzyme is a member selected from the group consisting of lipases, proteases, amylases, and mixtures thereof.
10
3. A composition according to Claim 1 wherein the organic solvent is a member selected from the group consisting of the monomethyl-, monoethyl-, monopropyl-, and monobutylethers of propoxylated propanol, and mixtures thereof.
4. A composition according to Claim 1 wherein the polyacrylate emulsifier has a
15 molecular weight in the range from 100,000 to 10,000,000.
5. A composition according to Claim 1 wherein the deterative surfactant is a member selected from the group consisting of amine oxides, alkyl ethoxy sulfates, and mixtures thereof.
- 20 6. A composition according to Claim 1 wherein the deterative surfactant is an ethoxylated alcohol or alkyl phenol
7. A composition according to Claim 1 or 3 which comprises at least 0.05%, by weight, of 1,2-octanediol.
25
8. A method for cleaning fabrics, comprising applying to said fabrics a composition according to Claim 1.
9. A method according to Claim 9 which is conducted in a hot air clothes dryer.
- 30 10. An article for cleaning fabrics, comprising an integral carrier containing a composition according to Claim 1.

International Application No
PCT/US 96/07448

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 D06L1/00 D06L1/02 D06L1/04 C11D3/386 C11D3/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 D06L C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,20 44 778 (CHEMISCHE WERKE HÜLS AG.) 16 March 1972 see the whole document ---	1,2,6,8
X	US,A,3 776 693 (SMITH G. N. ET AL.) 4 December 1973 see the whole document ---	1,2,6,8
A	FR,A,1 231 612 (AMERICAN CYANAMID CO.) 30 September 1960 see page 2, left-hand column, paragraph 4 see claims ---	1,2
A	DE,A,19 25 047 (ZSCHIMMER & SCHWARZ) 19 November 1970 see claim 1 --- -/--	1,6

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

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- * & * document member of the same patent family

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 328 174 (THE PROCTER & GAMBLE CO.) 16 August 1989 see page 3, line 9 - line 35 see claims 1,2 ---	1,3,6
A	US,A,4 692 277 (SIKLOSI MICHAEL P.) 8 September 1987 cited in the application see table 1 see claims 1-8 ---	1,7
A	US,A,5 055 215 (MAINS HAROLD E. ET AL.) 8 October 1991 see claims ---	10
A	EP,A,0 429 172 (UNILEVER PLC.) 29 May 1991 cited in the application see the whole document ---	8-10
A	US,A,5 238 587 (SMITH JAMES A. ET AL.) 24 August 1993 cited in the application see the whole document -----	8-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/07448

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A-2044778	16-03-72	NONE	
US-A-3776693	04-12-73	NONE	
FR-A-1231612	30-09-60	NONE	
DE-A-1925047	19-11-70	NONE	
EP-A-0328174	16-08-89	AU-B- 629529	08-10-92
		AU-A- 2890689	03-08-89
		CA-A- 1330927	26-07-94
		DE-D- 68914487	19-05-94
		DE-T- 68914487	06-10-94
		IE-B- 62760	22-02-95
		JP-A- 2147700	06-06-90
		US-A- 4966724	30-10-90
US-A-4692277	08-09-87	AU-B- 603558	22-11-90
		AU-A- 6681186	25-06-87
		CA-A- 1332909	08-11-94
		DK-B- 169133	22-08-94
		EP-A- 0227195	01-07-87
		GB-A, B 2184453	24-06-87
		HK-A- 50693	04-06-93
		JP-A- 62240392	21-10-87
US-A-5055215	08-10-91	US-A- 5196132	23-03-93
EP-A-0429172	29-05-91	AU-B- 629055	24-09-92
		AU-A- 6459490	18-04-91
		CA-A- 2027148	17-04-91
		JP-A- 3130473	04-06-91
US-A-5238587	24-08-93	CA-A- 2135746	25-11-93
		EP-A- 0640156	01-03-95
		JP-T- 7509629	26-10-95
		WO-A- 9323603	25-11-93